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INVESTIGATION OF THE ABSORPTION OF INFRARED RADIATION BY ATMOSPHERIC GASES: WATER, NITROGEN, NITROUS OXIDE

by

Darrell E. Burch
David A. Gryvnak
John D. Pembrook

Philco-Ford Corporation
Aeronutronic Division
Ford Road
Newport Beach, California 92663

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Principal Investigator and
   Telephone No. . . . . Dr. Darrell E. Burch
                                         (714) 833-1611

Project Scientist or Engineer and
   Telephone No. . . . . Dr. Robert A. McClatchey
                                         (617) 961-3224
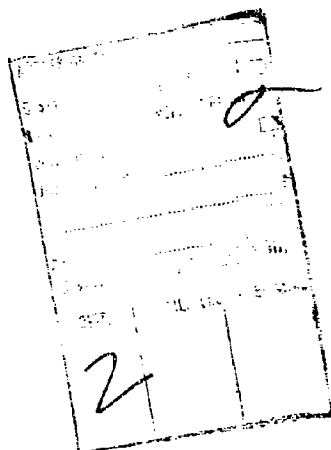
INVESTIGATION OF THE ABSORPTION OF
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Newport Beach, California 92663

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ABSTRACT

The continuum absorption by H_2O between 2400 and 2820 cm^{-1} and by N_2 between 2400 and 2650 cm^{-1} has been measured. The H_2O data cover the temperature range from 338 K to 428 K and are primarily for pure H_2O. A few preliminary results for $H_2O + N_2$ mixtures are discussed. Calculated values of the continuum-absorption coefficient are compared with the experimental results. From absorption data on samples of pure N_2 and of $N_2 + O_2$ at different temperatures, the attenuation by atmospheric N_2 has been calculated for a range of temperatures encountered in the atmosphere. The strengths of several N_2O bands between 1100 and 660 cm^{-1} have been measured and are tabulated.

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SECTION 1

INTRODUCTION AND SUMMARY

Several gases including H_2O, CO_2, CH_4, and N_2O contribute to the relatively small amount of absorption in the atmospheric window between 2400 cm^{-1} and 2900 cm^{-1}. Sections 2 and 3 deal with the absorption by two of these gases, H_2O and N_2, respectively, over a portion of this window from approximately 2400 cm^{-1} to 2820 cm^{-1}. By using a multiple-pass absorption cell[1] heated to 338 K with a path length of 949 m, we have been able to observe several H_2O lines that have not been seen previously. These lines have not been seen in long atmospheric paths because of interference with lines of other atmospheric gases. Throughout this region, H_2O contributes a small amount of continuum absorption that is probably due to the extreme wings of very strong lines centered several-hundred cm^{-1} away. Data on the H_2O continuum are presented in Section 2 for three temperatures, 338 K, 384 K,[2] and 428 K.

A pressure-induced band of N_2 contributes significantly to the atmospheric absorption between 2400 and 2600 cm^{-1}. By studying samples of pure N_2 and $N_2 + O_2$ over a wide range of temperatures, we have derived curves that relate absorption by atmospheric N_2 to path length for the temperature range ordinarily encountered in the atmosphere.

Section 4 summarizes the results of measurements of the strengths of several N_2O bands. Accurate values of the strengths are required in order that line-by-line methods can be used to calculate the absorption.

The absorber thickness, u, of a gas sample is given by

$$u(\text{molecules/cm}^2) = 2.69 \times 10^{19} \, p^*(\text{atm}) \, L(\text{cm}) \, (273/\theta)$$

$$= 7.34 \times 10^{21} \, p^* \, L/\theta \tag{1-1}$$

1-1

The temperature θ is in degrees Kelvin, and L is the geometrical path length through the sample. The density-equivalent-pressure p^* of the absorbing gas approaches its pressure p at low pressures. Because of the non-linear relationship between the density and the pressure of a gas, p^* may differ significantly from p at high pressures. For the gases and pressures used in the present investigation, the following expression is sufficiently accurate: $p^* = p(1 + c\,p)$. The pressures are in atm and, near room temperature, $c = 0.005$ for N_2O, and 0.001 for N_2 and O_2. For the largest N_2O samples studied, p^* is only approximately 5 percent greater than p; in all the pure H_2O samples and many of the others, the difference is negligible. In the following discussion certain quantities are said to be proportional to pressure; it should be borne in mind that the more correct quantity, density-equivalent pressure p^*, was used in the calculations where the difference between p^* and p was significant.

The true transmittance that would be observed with infinite resolving power is given by

$$T' = \exp(-u\kappa), \qquad \text{or} \qquad (-1/u)\ell_n T' = \kappa, \tag{1-2}$$

where κ is the absorption coefficient. Because of the finite slitwidth of a spectrometer and possible variations in κ with wavenumber due to line structure, the observed transmittance T may differ from T' at the same wavenumber. The quantity T represents a weighted average of T' over the interval passed by the spectrometer.

The intrinsic absorption coefficient due to a single collision-broadened absorption line at a point within a few cm^{-1} of the line center, v_o, is given by the Lorentz shape:

$$k = \frac{S}{\pi}\frac{\alpha}{(v-v_o)^2 + \alpha^2}. \tag{1-3}$$

The line strength $S = \int k\,dv$ is essentially independent of pressure for the conditions of the present study. It has been shown[2,3] that for $|v-v_o|$ greater than a few cm^{-1}, the Lorentz equation may require modification by a factor of X, which is a function of $(v-v_o)$. Therefore, Eq. (1-3) becomes

$$k = k_L = \frac{S}{\pi}\frac{\alpha\,X}{(v-v_o)^2 + \alpha^2}, \tag{1-4}$$

where k_L denotes the value given by the Lorentz equation. The value of X is approximately equal to unity for small $|v-v_o|$, but may be quite different for large $|v-v_o|$.

The half-width α is proportional to pressure so that k is, in turn, proportional to pressure in the extreme wings where $|v-v_o| \gg \alpha$. In some of the atmospheric windows, a significant portion of the absorption is due to

the extreme wings of strong lines whose centers are several cm^{-1} away. An example is the H_2O continuum between 2400 and 2820 cm^{-1} that is discussed in Section 2. It follows from Eq. (1-4) that the wing-absorption coefficient C_w due to the extreme wings of several lines is equal to the sum of all the k^w's due to the individual lines and is proportional to pressure, ($C_w = C_w^0 p^*$). Since wing absorption changes slowly with wavenumber, it is frequently called continuum absorption.

Another type of continuum absorption arises from pressure-induced bands; the absorption coefficient, C_p, for pressure-induced absorption is also proportional to pressure. The N_2 absorption discussed in Section 3 is pressure induced since an N_2 molecule is not infrared active unless it is perturbed by neighboring molecules. The absorption coefficient due to local lines whose centers occur within a few cm^{-1} of the point of observation is denoted by κ(local). This quantity may vary rapidly with wavenumber and depends on pressure as indicated by Eq. (1-3) because of collision-broadening of the absorption lines.

At a given wavenumber, there may be appreciable absorption due to local lines, the wing continuum, the pressure-induced continuum, or to any of these three. Therefore, the total absorption coefficient κ in Eq. (1-2) may be given by

$$\kappa = \kappa(local) + C_w + C_p . \qquad (1-5)$$

For a sample of absorbing gas only, such as the pure H_2O samples discussed in Section 2, we can rewrite Eq. (1-5) as

$$\kappa = \kappa(local) + (C_{s,w}^0 + C_{s,p}^0) p^* , \qquad \text{(absorbing gas only)} \qquad (1-5a)$$

where the normalized coefficients $C_{s,w}^0$ and $C_{s,p}^0$ are the values of C_w and C_p, respectively, when $p^* = 1$. The subscript s denotes self-broadening of the lines or self-induced absorption. Since u is proportional to p^*L, ($-\ell_n T$) due to wing continuum or pressure-induced continuum is proportional to $p^{*2}L$.

Samples frequently contain a non-absorbing gas along with the absorbing gas. This gas broadens the absorption lines and may induce additional absorption by the pressure-induced bands of the absorbing gas. For a mixture of an absorbing gas and a broadening gas, Eq. (1-5a) becomes

$$\kappa = \kappa(local) + (C_{s,w}^0 + C_{s,p}^0) p^* + (C_{b,w}^0 + C_{b,p}^0) p_b^* . \qquad (1-5b)$$

$C_{b,w}^0$ and $C_{b,p}^0$ are the normalized coefficients for wing absorption and pressure-induced absorption by the absorbing gas due to the presence of the broadening gas denoted by subscript b. A particular broadening gas is designated by its symbol rather than by b. The N_2O measurements reported in Section 4 were made at wavenumbers where the intrinsic absorption by the

nearly, or local, lines is much greater than the continuum absorption. Thus, ... the absorption coefficient κ is equal to κ(local), which is the sum of the coefficients due to all of the local lines contributing at that wavenumber.

If all of the absorption in a given spectral region is due to a single intrinsic absorption band, the band strength, which is the sum of the strengths of all the lines, is given by

$$S = \int \kappa d\nu = (-1/u) \int \ell n T' \, d\nu . \tag{1-6}$$

This quantity is also frequently called band intensity or integrated absorption coefficient. If two or more bands occur in the spectral region, the quantity on the right-hand side of Eq. (1-6) represents the sum of the strengths of the bands. Because of the finite slitwidth of a spectrometer, the observed transmittance T may be quite different from T'. However, if the absorption lines are sufficiently wide that variations in κ are not too great within the spectral slitwidth, $-\int \ell n T d\nu$ closely approximate $-\int \ell n T' d\nu$, where the integration is performed over the entire band. Under this condition, S can be determined from the measurable quantity T by substituting T for T' in Eq. (1-6). Systematic errors due to differences between T and T' are usually such that $(-\ell n T)$ is less than $(-\ell n T')$. Although some structure may remain in the spectrum, i.e., κ may vary rapidly with changing wavenumber, $-\int \ell n T d\nu$ closely approximates $-\int \ell n T' d\nu$ if $(1-T') \ll 1$ at all wavenumbers. This condition corresponds to the so-called linear region of absorption and requires that the average absorption over a band is only a few percent, and thus difficult to measure accurately. For N_2O samples at about 10 atm or more, the ratio of the line widths to their spacings is sufficiently large that most of the structure is smoothed out. Therefore, the transmittance T observed by a spectrometer with spectral slits of a few tenths of a cm^{-1} closely approximates T'. In the study of N_2O we used sample pressures of several atm and substituted T for T' in Eq. (1-6) to determine the band strengths. By using the high pressures, we could use samples with absorptance as much as 90 percent without introducing significant errors due to differences between T and T'.

SECTION 2

H_2O ABSORPTION BETWEEN 2400 and 2820 cm^{-1}

Each of the N_2O, CO_2 and CH_4 bands in the 2400-2900 cm^{-1} window has been studied individually in absorption cells with the gas concentration much higher than it is in the atmosphere. Studying the H_2O absorption in this region is much more difficult since the H_2O vapor pressure is limited to only a few-hundredths of an atmosphere unless the cell is heated well above room temperature. The absorption lines are weak so that large samples are required in order to produce measurable absorption. The overlapping bands of other gas species complicate studies of the atmosphere. These diffi- culties account to a large degree for the lack of knowledge about the H_2O absorption in this region.

We have used both of our multiple-pass absorption cells to contain samples of pure H_2O and H_2O + N_2. The 949 m path length available with the longer cell made it possible to use sufficiently large absorber thicknesses at relatively low pressures to observe many H_2O lines that can not be seen in an atmospheric spectrum. The long cell was heated to 338 K to permit higher H_2O pressures; the maximum pressure employed was 0.13 atm. The shorter absorption cell is capable of higher temperatures and was used up to 428 K with H_2O pressures as high as 3 atm. Two representative spectral trans- mittance curves are shown in Fig. 2-1. The spectral resolution varies from approximately 0.23 cm^{-1} at 2400 cm^{-1} to 0.32 cm^{-1} at 2650 cm^{-1} for sample 4MH40. Spectral slits approximately 60 percent wider were used while scan- ning sample 4MH69. The weak lines in the spectrum of sample 4MH40 are more prominent because of the longer path and lower pressure. Much of the struc- ture is smoothed in the spectrum of sample 4MH69 by the higher pressure which broadens the lines so that their halfwidths are between 0.4 and 0.8 cm^{-1}. Table 2-1 at the end of this Section contains a listing of values of the integrated absorptance, $\int A(\nu)\, d\nu$, for these samples ($A(\nu) = 1 - T(\nu)$).
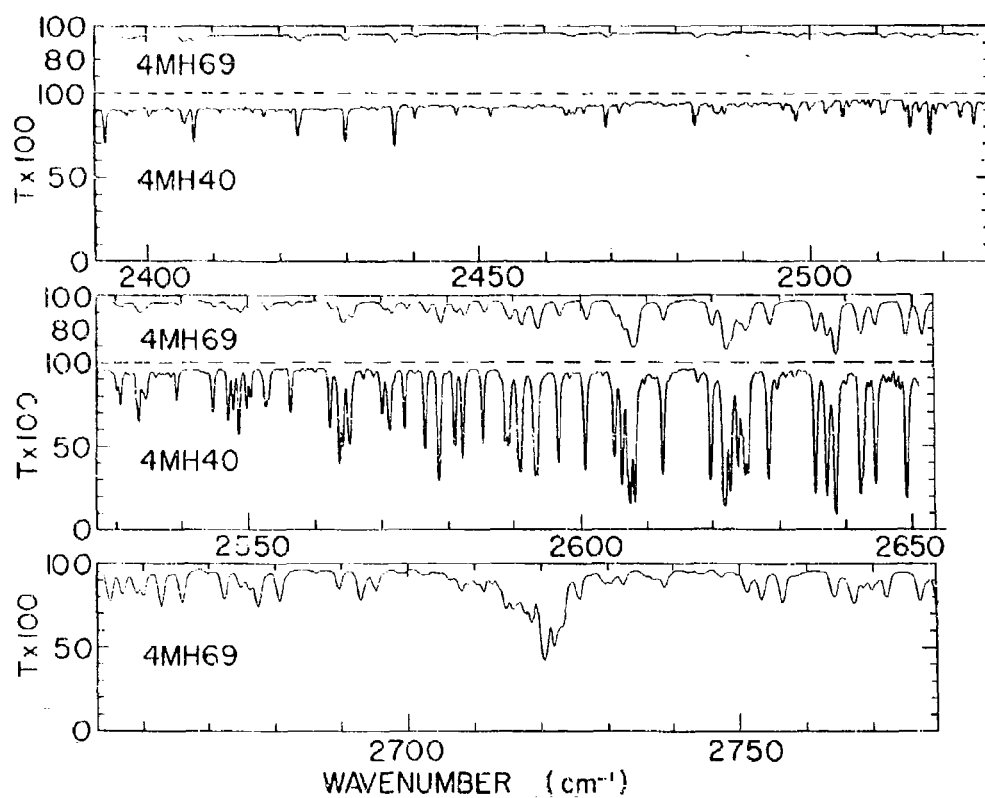
FIG. 2-1. Spectral transmittance curves of H_2O between 2392 cm^{-1} and 2780 cm^{-1}. The sample parameters are:

Sample	Temp. (K)	L (m)	p (atm)	u (molecules/cm^2)
4MH69	383	32.9	0.758	4.78 x 10^{22}
4MH40	338	949	0.125	2.58 x 10^{23}

Several short sections of the spectral curve for sample 4HM40 show maximum transmittance and have no apparent lines over intervals of 3 or 4 cm^{-1}. Most of the absorp   on at these points is probably due to continuum which arises from the extreme wings of very strong lines centered a few hundred cm^{-1} away. The continuum was studied by measuring the absorption at the following wavenumbers of maximum transmittance: 2402.5, 2427.6, 2442.5, 2477.1, 2493.1, 2527.9, 2559.5, 2587.3, 2602.8, 2615.7, 2627.2, 2669, 2732.3 and 2826 cm^{-1}. Measurements of the continuum are especially important because so little is known about the shapes of the extreme wings of lines that it cannot be calculated accurately.

The accuracy of our continuum measurements is somewhat less than we had anticipated. Accurate measurements of continuum absorption by large samples are difficult under the best conditions; adsorption and condensation make H_2O measurements even more difficult. Determining the 100 per-cent-transmittance curve on a spectral curve is subject to error since the accuracy depends on stability of the optical and electrical components while a sample is put in the cell and the spectral interval is scanned. With large, multiple-pass cells, the alignment of the mirrors inside the cell is always somewhat sensitive to changes in pressure or temperature. Since large samples are required, a trace of an impurity gas that absorbs in the region of interest can also produce errors. The experiment on H_2O continuum had some additional problems that we believe arose from changes in the reflectivity of the mirrors in the cell that occurred when the amount of H_2O vapor was varied.

Two different methods were used to obtain data with the small multiple-pass cell. In the first method, a sample of H_2O vapor was placed in the cell and several short spectral intervals were scanned including the wavenumbers of maximum transmittance. Additional H_2O was added to the sample and the process was repeated for four or five different pressures. Three to four hours were required for the series of measurements. In the second method, the sample was added to its maximum pressure as quickly as possible and the transmittance was measured at a fixed wavenumber for four or five pressures as the pressure was decreased. Only 15 to 20 minutes were re-quired to make the series of measurements at a single wavenumber.

Results obtained by the two methods did not agree as well as expected. Most of the difference can probably be attributed to the length of time a sample was in the cell before its transmittance was measured. We found in another type of measurement that the transmitted signal decreased slowly for several hours after a sample had been put in the cell. We attributed at least part of this anomalous absorption to a film formed on the mirror surfaces. When the cell was evacuated, the transmitted signal continued to increase slowly at some wavenumbers for several minutes after the pres-sure was sufficiently low that absorption by the H_2O vapor was negligible. It seems probable that the slow change in transmitted energy after a sample had been added or removed was due to a change in a film on the mirror surfaces.

Because of the shorter time between the introduction of the sample and the transmittance measurement, data obtained by the second method described in the previous paragraph are probably more accurate. Therefore, none of the data obtained with the short cell by the first method were used in the final analysis. The amount of anomalous absorption was much greater between 2650 and 3000 cm^{-1} than between 2400 and 2650 cm^{-1}.

Much of the anomalous absorption disappeared after the cells had been evacuated for several minutes; however, some persisted after days of evacuation. A typical background curve obtained with the long absorption cell evacuated was smooth between 2400 and 2650 cm^{-1}, but showed some apparent absorption between 2650 and 3000 cm^{-1}. The curve displayed four broad minima at about 2720, 2870, 2935, and 2970 cm^{-1}. At these points, the curves fell from 10 to 20 percent below the expected smooth curve with the cell adjusted to 32 passes. At 4 passes, the apparent absorption was much less, indicating it was associated with the mirrors rather than the windows. The amount of apparent absorption decreased, but did not disappear after the mirrors were cleaned. A similar deviation from a smooth background curve was also observed between 2800 and 3000 cm^{-1} with the short absorption cell. Below 2800 cm^{-1}, the background curve was smooth.

Determining the continuum coefficients for pure H_2O involved the application of Eqs.(1-2) and (1-5a) to transmittance values observed at the points of maximum transmittance listed above. Although knowing the source of the continuum is not important in the analysis, we assumed that it results from wing absorption and use the subscript w in accordance with the discussion in Section 1. We plotted values of $(-1/u)\ell n\,T$ vs p at a given wavenumber for a fixed temperature and path length. In accordance with the discussion of Eq.(1-5a), we would expect the plotted points to fall on a straight line that intersects the p = 0 line at κ(local) and has a slope equal to $C_{s,w}^o$. Two such plots are shown in Fig. 2-2.

The lower panel of Fig. 2-2 represents data for samples at 428 K. The anomalous absorption was not serious at 2402.5 cm^{-1} for this temperature, as can be seen in the figure. The straight line fits the points well and passes near the origin. This result is expected for continuum absorption with little contribution due to local lines. Similar results were obtained at other wavenumbers and for samples at 384 K. Samples represented in the upper panel were contained in the long cell with 0.13 atm maximum pressure. We note that the intercept of the curve with the p = 0 line is greater in the upper panel than in the lower panel. The value of this intercept gives κ(local) according to Eq. (1-5a) if no anomalous absorption is present. The greater value of κ(local) at the lower temperature, as indicated by the figure, is unrealistic. We attribute the unusually high intercept with the p = 0 line in the upper panel to the anomalous absorption discussed above. Typically, the points corresponding to 338 K fell on a straight line with an expectedly high intercept. Thus, we could not determine a reliable value for κ(local). We assumed that $C_{s,w}^o$ was
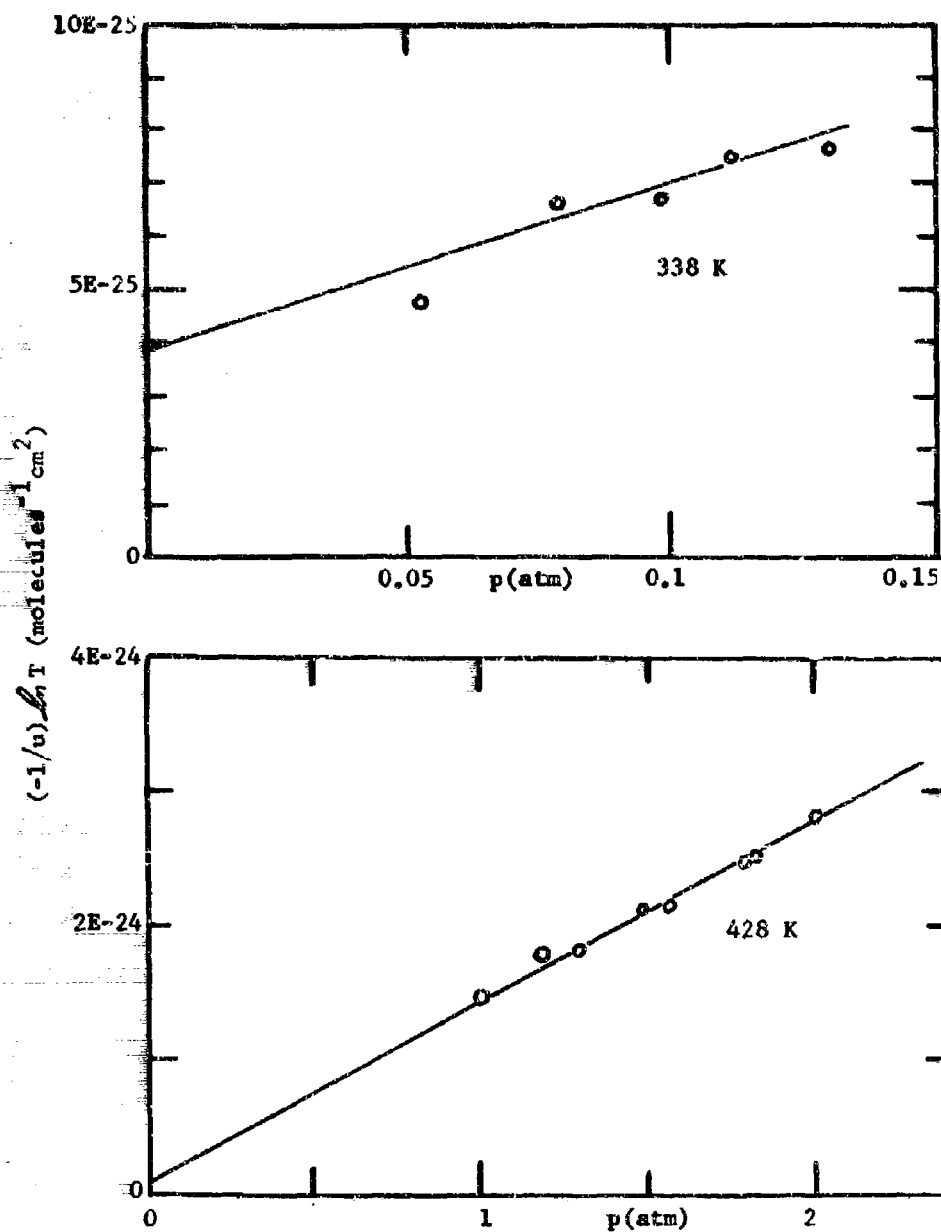
FIG. 2-2. Plots of $(-1/u)\ln T$ vs p at 2402.5 cm^{-1} for H_2O at 338 K and 428 K.

still given by the slope of the curve. This assumption is equivalent to the assumption that the anomalous absorption was proportional to the H_2O pressure.

The values of $C_{s,w}^o$ determined by the methods described above are plotted vs wavenumber in Fig. 2-3 for the three temperatures at which data were obtained. Also included in the figure is a plot corresponding to 296 K that was obtained in the following manner. Values of $C_{s,w}^o$ for the three elevated temperatures were plotted for 5 different wavenumbers on a semi-logarithmic scale vs $1/\theta$, where θ is the temperature in K. The curves are shown in Fig. 2-4. The points corresponding to a given wavenumber fall on a straight line, implying that $C_{s,w}^o$ is proportional to exp (constant$/\theta$) within the experimental uncertainty. The curves were extrapolated to points corresponding to 296 K, and the values at this temperature were plotted in Fig. 2-3. However, in the spectral region between 2650 and 2820 cm^{-1} data were obtained for only one temperature, 384 K, so that the method used to extrapolate to 296 K cannot be applied in this region. The anomalous absorption between 2650 and 2820 cm^{-1} was less at 384 K than at the other temperatures. The values of $C_{s,w}^o$ at 384 K for the 2650-2820 cm^{-1} region all fell within the range of values observed at the lower wavenumbers. In order to determine a value for the 296 K curve between 2650 and 2820 cm^{-1}, we found a wavenumber between 2400 and 2650 cm^{-1} for which $C_{s,w}^o$ for 384 K was the same as at the wavenumber of interest for the same temperature. We then assumed that $C_{s,w}^o$ was also the same at these two wavenumbers at 296 K. The estimated uncertainty is $\pm$ 20 percent for the two curves at 384 K and 428 K, and $\pm$ 30 percent for the two curves corresponding to lower temperatures.

Influence of Nitrogen Broadening on the Continuum

The earth's atmosphere contains much more N_2 and O_2 than H_2O so that the broadening of H_2O lines by N_2 and O_2 is generally more important than the self-broadening. Since the continuum absorption coefficient $C_{N,w}^o$ is very small throughout the 2400-2820 cm^{-1} region, samples consisting of large absorber thicknesses and high N_2 pressures are required in order to measure this quantity. The short, multiple-pass-cell was used for this purpose since it can be operated at higher pressures and at higher temperatures, which permits greater absorber thicknesses, than the long cell. All of the measurements with N_2 were at 428 K. No data were obtained with O_2. Since only about 20% of the atmosphere consists of O_2, it is probably safe to assume that the continuum absorption coefficient for this gas is the same as for N_2 when calculating atmospheric transmittance.

In a typical measurement, the spectrometer was adjusted to one of the narrow windows where the continuum absorption dominates over the local-line absorption. Two atm of H_2O vapor was introduced to the cell; then N_2 was added to produce total pressures of 4.5, 5.7, 7.5 and 10 atm. The transmittance was measured at each pressure after the sample had mixed for several minutes.
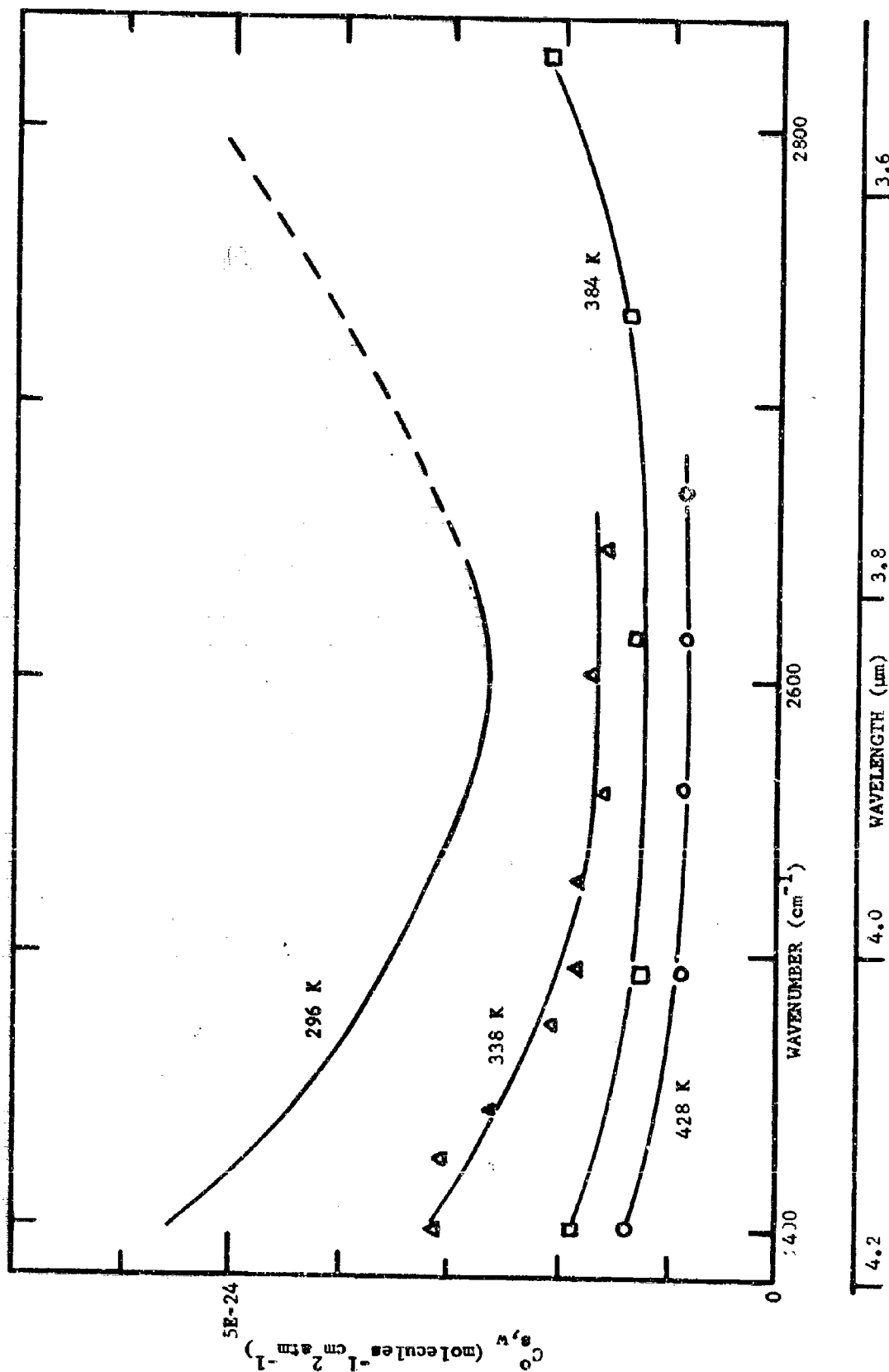
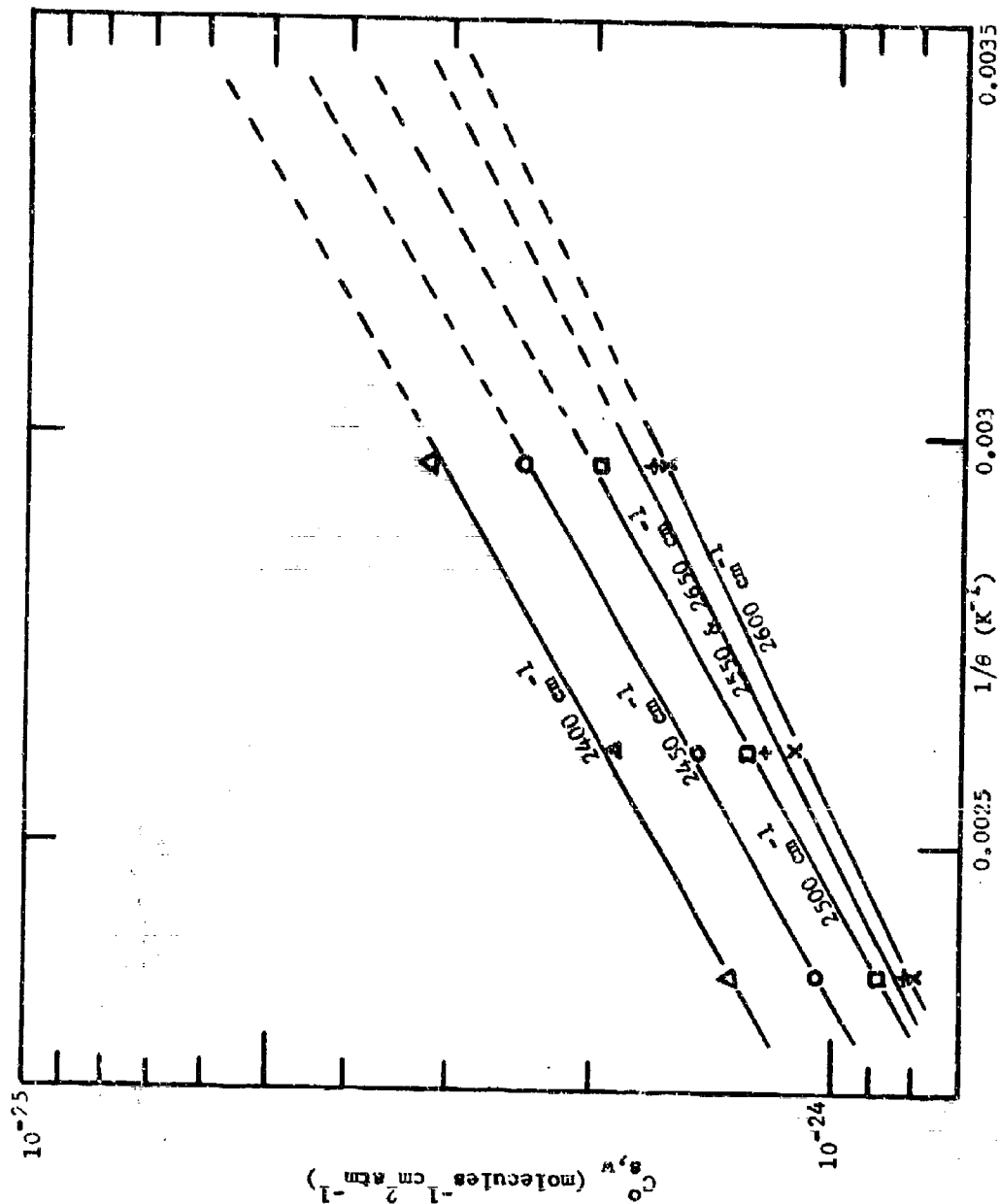FIG. 2-3. Spectral plots of $C_{s,w}^o$ between 2400 and 2820 cm^{-1} for H_2O at four temperatures.

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FIG. 2-4. Semi-logarithmic plots of $C_{s,w}^{o}$ vs $1/\theta$ for 6 different wavenumbers. The curves $C_{s,w}^{o}$ for 2550 and 2650 wavenumbers are essentially coincident.

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The total operation for all pressures required between 1 and 1.5 hours. We plotted $(-1/u)$ $(\ell_n T - \ell_n T'')$ vs p_{N_2}, where T'' is the transmittance of the pure H_2O sample. In accordance with Eq. (1-5b), the points fell on a straight line drawn through the origin; the slope determined the value of $C^o_{N,w}$. Similar measurements were made at four wavenumbers, 2393, 2560, 2616 and 2667 cm^{-1}. At 2393 cm^{-1}, a significant portion of the absorption by the $H_2O + N_2$ samples was due to pressure-induced absorption by N_2. Data presented in Section 3 were used to account for the N_2 absorption.

After accounting for the pressure-induced N_2 absorption and the anomalous absorption, we concluded that the ratio of $C^o_{N,w}/C^o_{s,w} = 0.12 \pm 0.03$. This result is in fair agreement with that of Palmer[4], who found the corresponding ratio varied from approximately 0.09 to 0.17 at points in the windows between the lines in the 25-50 cm^{-1} region. In some previous work[5], we found this ratio to be much smaller, probably less than 0.005, for corresponding points between 800 and 1200 cm^{-1}. In the latter region, the lines contributing most to the continuum may be centered further from the points of observation than is the case in the 2400-2800 cm^{-1} region. This may account for the difference in the values of the ratio.

Unfortunately, $C^o_{N,w}$ cannot be measured accurately in the 2400-2820 cm^{-1} region with samples at temperatures as low as those commonly occurring in the atmosphere. Until additional data are available, we recommend values of $C^o_{N,w}$ for temperatures near 296 K that are determined by multiplying values of $C^o_{s,w}$ at 296 K from Fig. 2-3 by 0.12, the ratio observed at 428 K. The values of $C^o_{s,w}$ and $C^o_{N,w}$ determined in this manner can be used to calculate the continuum due to atmospheric H_2O if the total pressure is used as p_{N_2}.

Comparison Between Observed and Calculated Continuum

It is of interest to compare the continuum with calculated values based on published values of the strengths and widths of the strong H_2O lines. The parameters for lines centered between 2900 cm^{-1} and 4000 cm^{-1} are based on Gates, et al.[6], those centered below 1000 cm^{-1} and 2400 cm^{-1} on Calfee and Benedict[7]. The self-broadened H_2O lines were assumed to be five times as wide as N_2-broadened H_2O lines at the same pressures in accordance with previous work. The calculated value for $C^o_{s,w}$ at 2400 cm^{-1} and 338 K is 4.1×10^{-24} atm^{-1} molecules^{-1} cm^2 for the Lorentz line shape and 7.8×10^{-24} atm^{-1} molecules^{-1} cm^2 for the Gross[8] line shape given by the following equation:

$$ k = \frac{S}{\pi} \frac{4\nu^2 \alpha}{(\nu^2 - \nu_o^2)^2 + 4\alpha^2 \nu^2} \cdot \tag{2-1} $$

These calculated values for self-broadening are in fair agreement with the observed value 3.1×10^{-24} atm^{-1} molecules^{-1} cm^2. The calculated value

of $C_{N,w}^O$ for N_2 broadening is 0.2 $C_{s,w}^O$, since the self-broadened lines are five times as wide as the N_2-broadened lines.

The curves in Fig. 2-3 indicate a large decrease in the $C_{s,w}^O$ with increasing temperature. This result is consistent with our previous work on the H_2O continuum between 8 and 13 μm. Such a strong dependence on temperature cannot be explained by simple theories on the shapes of collision-broadened lines.

TABLE 2-1

INTEGRATED ABSORPTANCE FOR H_2O

$$\int_{2392}^{\nu} A(\nu)\ d\nu\ (cm^{-1})$$

Sam. No. ν (cm^{-1})	4MH69	4MH40	Sam. No. ν (cm^{-1})	4MH69	4MH40	Sam. No. ν (cm^{-1})	4MH69	4MH40
2392	0.000	0.000	2515	7.280	11.38	2640	18.008	33.015
2395	0.237	0.403	2520	7.596	11."G	2645	18.635	34.450
2400	0.586	0.931	2525	7.872	12.31.	2650	19.113	35.425
2405	0.912	1.445	2530	8.116	12.620	2655	19.683	
2410	1.305	2.077	2535	8.485	13.402	2660	20.407	
2415	1.609	2.564	2540	8.742	13.829	2665	21.021	
2420	1.913	3.076	2545	8.981	14.226	2670	21.475	
2425	2.263	3.683	2550	9.358	14.993	2675	21.987	
2430	2.569	4.228	2555	9.672	15.545	2680	22.669	
2435	2.871	4.736	2560	9.917	15.896	2685	23.108	
2440	3.200	5.282	2565	10.344	16.836	2690	23.459	
2445	3.482	5.718	2570	10.684	17.468	2695	24.007	
2450	3.756	6.156	2575	11.069	18.283	2700	24.358	
2455	4.038	6.626	2580	11.523	19.216	2705	24.654	
2460	4.294	7.048	2585	11.904	19.969	2710	25.197	
2465	4.569	7.543	2590	12.314	20.921	2715	25.920	
2470	4.859	8.019	2595	12.938	22.362	2720	27.327	
2475	5.125	8.390	2600	13.253	23.004	2725	29.181	
2480	5.370	8.734	2605	13.616	23.759	2730	29.737	
2485	5.653	9.153	2610	14.576	25.883	2735	30.164	
2490	5.922	9.603	2615	14.915	26.642	2740	30.629	
2495	6.156	9.937	2620	15.232	27.263	2745	30.898	
2500	6.439	10.369	2625	16.257	29.461	2750	31.202	
2505	6.711	10.742	2630	16.768	30.650	2755	31.844	
2510	6.981	11.038	2635	17.022	31.019	2760	32.362	
						2765	32.794	
						2770	33.524	
						2775	34.050	
						2780	34.721	

SECTION 3

ATMOSPHERIC ABSORPTION BY N_2 BETWEEN 2400 and 2640 cm^{-1}

In a previous report[9] we presented data on the pressure-induced absorption by N_2 between 2400 and 2640 cm^{-1}. Since the time the previous report was published, we have made some additional measurements at elevated temperatures in order to determine the temperature dependence of the absorption. We have also repeated some of our previous measurements at room temperature and made some additional ones with a 949 meter path length and samples up to 2.5 atm. Our recent results agree very well with our previous ones. In order that this report be complete, we are including some of the previous results along with the recent ones.

Shapiro and Gush[10] have published spectral data on N_2 absorption for samples at approximately 20 atm pressure. Farmer and Houghton[11] have also measured the absorption between 2400 cm^{-1} and 2525 cm^{-1} by approximately 1 atm of pure N_2 with path lengths of a few hundred meters. The results of Farmer and Houghton are consistent with the data obtained at high pressures by Shapiro and Gush if $(-\ln T)$ is assumed to be proportional to p^2L, according to the discussion following Eq.(1-5a). Our work was undertaken to check the previous work and to determine the influence of changing temperature. We also determined the coefficient $C^o_{O_2,p}$ for N_2 absorption induced by O_2. From the value of this coefficient and the corresponding coefficient, $C^o_{s,p}$, for self-induced absorption by N_2, we have calculated the transmittance by N_2 in the earth's atmosphere from approximately 2400 cm^{-1} to 2650 cm^{-1} for several temperatures.

Values of the absorber thickness of N_2 were calculated by use of Eq.(1-1). Since there is no absorption by N_2 other than that which is pressure induced, Eqs.(1-2) and (1-5b) combined to give

$$-\frac{1}{u} \ln T' = p^* C^o_{s,p} \qquad (3-1)$$

3-1

for a pure N_2 sample, and

$$-\frac{1}{u} \ln T' = p^* \, C_{s,p}^o + p_{O_2}^* \, C_{O,p}^o \qquad (3\text{-}1a)$$

for a sample of $N_2 + O_2$. Since the true transmittance T' changes slowly with wavenumber in continuum absorption, the observed transmittance T is essentially equal to T'. Note that $C_{O,p}^o$ corresponds to absorption by N_2 that is induced by O_2; the O_2 does not absorb in this spectral region. We detected no absorption by a sample of 8 atm of O_2 with a 32.9 meter path length. After values of $C_{s,p}^o$ had been found from pure N_2 samples we determined $C_{O,p}^o$ from data on $O_2 + N_2$ mixtures by use of Eq. (3-1a). The results for pure N_2 and for $O_2 + N_2$ mixtures at 296 K are summarized in Fig. 3-1. The good agreement among the pure N_2 data at different pressures provides evidence of the pressure dependence assumed in deriving Eq. (3-1). Below approximately 2500 cm^{-1}, our results for pure N_2 differ by less than $\pm$ 5 percent from those by Shapiro and Gush. At larger wavenumbers, the agreement is within the accuracy to which the curves of Shapiro and Gush can be read. Data obtained from samples of N_2 with 5 atm of O_2 compared well with data from samples of N_2 with 8 atm of O_2, indicating the validity of the term involving $p_{O_2}^*$ in Eq. (3-1a).

Fig. 3-2 summarizes the results for self-induced N_2 absorption at three different temperatures. A relatively strong temperature dependence is seen; at the lower wavenumbers the absorption coefficient decreases with increasing temperature, whereas the opposite appears to be true near the high wavenumber edge of the band. At the elevated temperatures, 380 K and 457 K, turbulence in the samples caused the measuring accuracy to be somewhat lower than at room temperature. For the elevated temperatures, the estimated uncertainty in the curves is approximately $\pm$ 0.05 x 10^{-26} molecules^{-1} cm^2 atm^{-1} above 2550 cm^{-1}. Near 2400 cm^{-1}, the uncertainty may be twice this large. We read values from the curves of Fig. 3-2 and cross-plotted them with $\ln C_{s,p}^o$ as the ordinate and $(1/\theta)$ as the abscissa, where θ is the temperature in degrees Kelvin. The three points corresponding to a given wavenumber deviated by no more than a few percent from a straight line. A few data obtained at 280 K, but not shown in Fig. 3-2, also fell on the line within the experimental accuracy.

The occurrence of the points on straight lines indicates that the coefficient can be related to temperature by an equation of the form

$$C_{s,p}^o (\theta) = A \exp (B/\theta) , \qquad (3\text{-}2)$$

over the ranges of temperature and wavenumber studied. Constants A and B are functions of wavenumber. We used the plots of $\ln C_{s,p}^o$ versus $(1/\theta)$ to determine values of $C_{s,p}^o$ at various temperatures which represent the earth's atmosphere. These values were used in the following manner to calculate the absorption by atmospheric N_2.
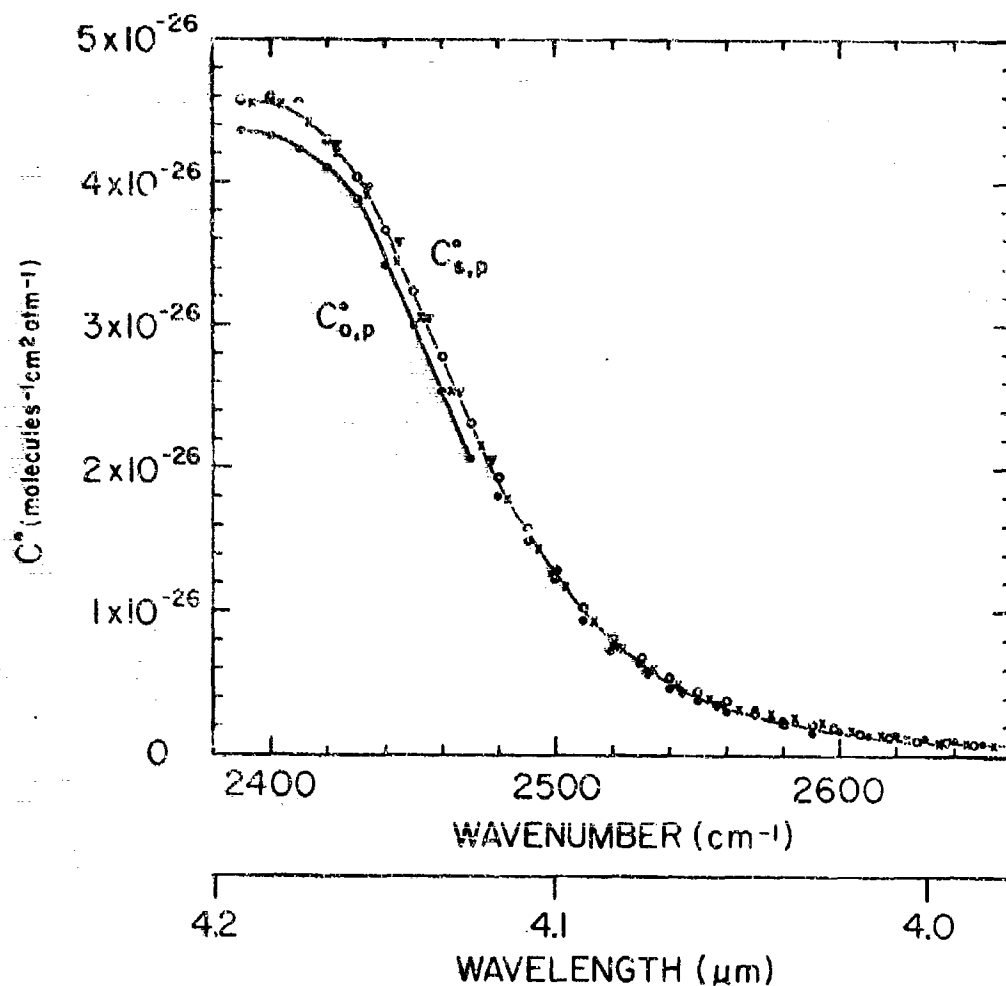
FIG. 3-1. Spectral plots of the normalized pressure-induced N_2 absorption coefficient. The upper curve represents $C_{s,p}^o$ and is based on pure N_2. The various geometrical figures correspond to samples of pure N_2: ∇, L = 36.9 m, p = 14.6 atm; x, L = 32.9 m, p = 13.6 atm; O, L = 32.9 m, p = 21.8 atm. Recent results based on samples at 1.5 and 2.5 atm but not plotted agree very well with points shown. The temperature is 296°K. The lower curve represents $C_{o,p}^o$ and is based on mixtures of approximately 14 atm N_2 + 8 atm O_2 with L = 32.9 m.
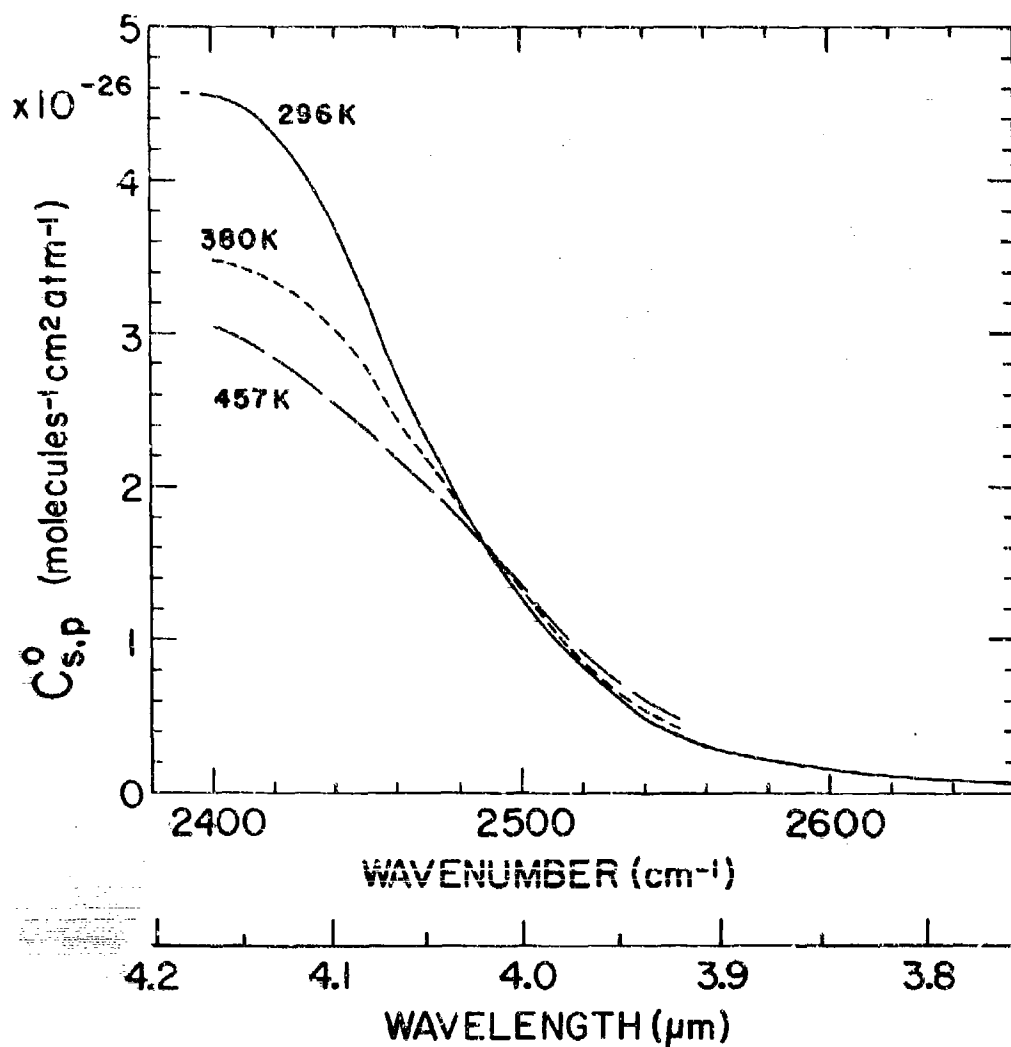
3-3

FIG. 3-2. Spectral plots of $C_{s,p}^{o}$ for pressure-induced N_2 absorption at three temperatures.

3-4

Air contains approximately 78 percent N_2, 21 percent O_2, and 1 percent other gases. For simplicity, we assumed that the miscellaneous gases comprising the 1 percent induce N_2 absorption as efficiently as O_2 so that the air is effectively 22 percent O_2 and 78 percent N_2. From Fig. 3-1, we see that $C^o_{O_2,p} = 0.95\ C^o_{s,p}$ over the region of strongest absorption at 296 K. We assumed that this relationship holds for all temperatures and wavenumbers of interest. Possible deviations from this relationship will probably not produce errors greater than a few percent in the calculated atmospheric absorption. By making this assumption, we can rewrite Eq.(3-1a) for an air path at P atm as follows:

$$-\ell n\,T = uP\ C^o_{s,p}\ [\ 0.78 + 0.95\ (0.22)\ ] = 0.99\ u\ P\ C^o_{s,p}\ . \tag{3-3}$$

At temperature θ, the thickness of N_2 in an atmospheric path of L km is

$$u(\text{molecules cm}^{-2}) = PL\ 2.69 \times 10^{24}\ (0.78)\ (273/\theta).$$

It follows that

$$\frac{-\ell n\,T}{P^2 L}\ (\text{atm}^{-2}\ \text{km}^{-1}) = \frac{5.67 \times 10^{26}}{\theta}\ C^o_{s,p} \tag{3-4}$$

for an atmospheric path. A slant path over which the pressure and/or temperature varies can be divided into layers each of which can be assumed to have constant temperature and pressure. The quantity $-\ell n\,T$ for the entire path is the sum of the corresponding quantities for the individual layers. The results of the calculations of the absorption by atmospheric N_2 are summarized in Fig. 3-3 for the four temperatures indicated. Near 2400 cm^{-1}, the attenuation per kilometer varies by nearly a factor of two over a temperature range corresponding approximately to extremes encountered in the earth's atmosphere. At higher wavenumbers, the attenuation and its variation with temperature change are too small to measure accurately. Therefore, only the 296K curve is shown at the high wavenumbers.
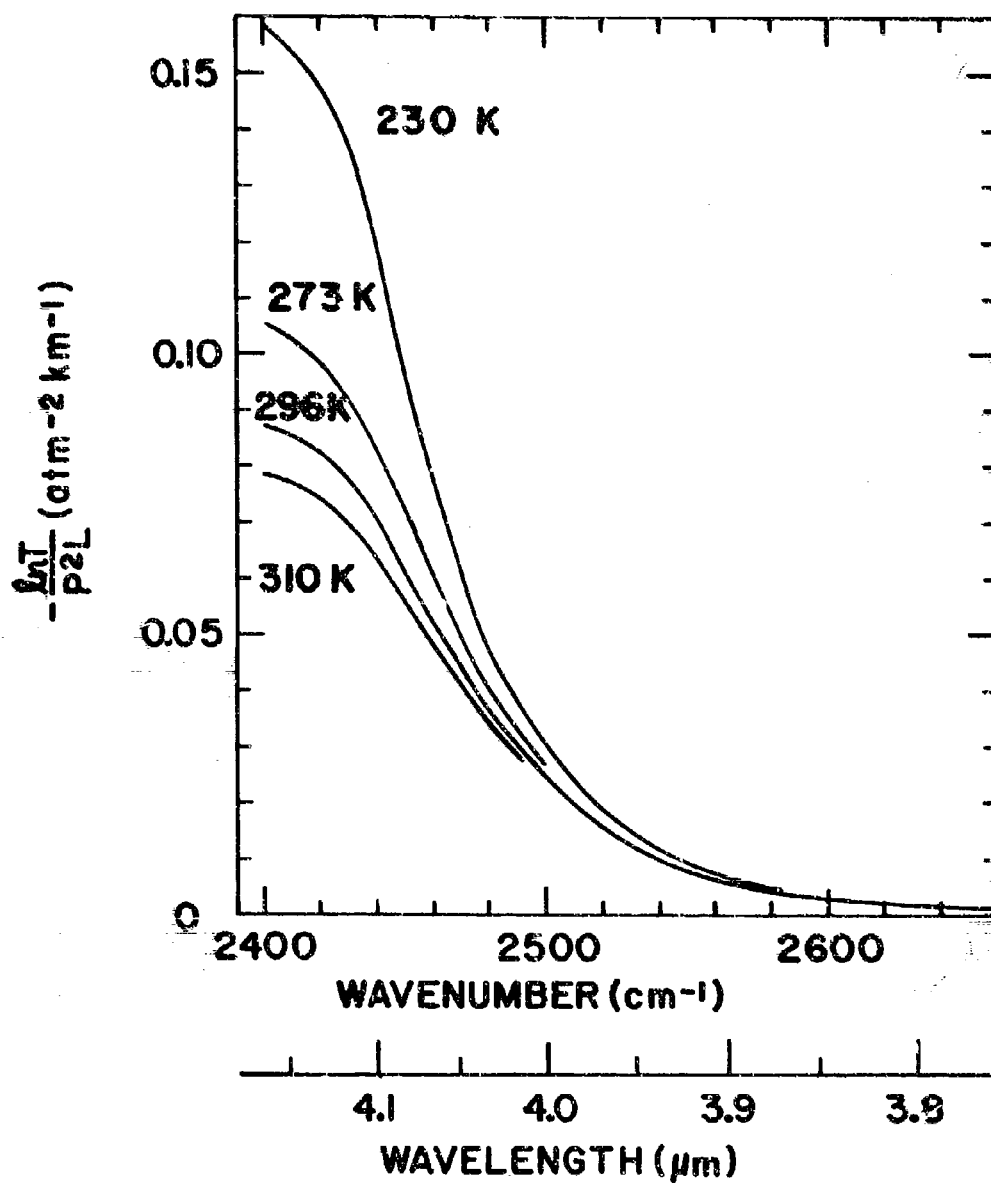
FIG. 3-3. Spectral plots of $([-\ell n\,T]/p^2L)$ for atmospheric N_2 at four temperatures.

3-6

SECTION 4

N_2O BAND STRENGTHS

The N_2O band systems near 1168, 1278, and 2224 cm^{-1} play an important role in atmospheric absorption since they occur in the window regions. In order to use line-by-line methods to calculate the absorption by these bands, their strengths must be known accurately. Various workers have measured the band strengths, but the results differ widely so that the proper values were still uncertain. Therefore, we decided to measure the strengths by using experimental techniques believed to be more reliable than some of those used previously. Two sources of error probably account for many of the discrepancies among previous results. The first is insufficient broadening of the lines as discussed in Section 1. The second source of errors results from using dilute mixtures of N_2O with a non-absorbing gas to produce high pressures while maintaining a sufficiently small absorber thickness. These errors become more serious for increasingly dilute mixtures because of improper mixing or selective adsorption by one of the gases on the walls of the cell or gas-handling system.

By using short absorption cells approximately 1 mm and 6 mm long, we were able to use pure N_2O samples or mixtures of $N_2O + N_2$ which were not too dilute for the N_2O pressure to be determined accurately. Other precautions were taken to avoid errors due to adsorption on the walls of the cell. Pressures from 8 to 15 atm broadened the absorption lines so that the structure was smoothed.

A few years ago, we scanned several spectral curves from which we recently determined the strengths of the stronger bands between 4000 and 6600 cm^{-1}. These bands are weaker than those at lower wavenumbers and contribute less to atmospheric absorption. The samples were contained in a multiple pass absorption cell with path lengths between 4 and 36 meters.

4-1

The strengths of the band systems at 296 K are summarized in Table 4-1 with values published by other workers. In accordance with the discussion following Eq.(1-6), values given in the Table are $(-1/u)\int \ell n\, T\, dv$, where the integration is performed over the spectral interval including essentially all of the lines. Each of the bands resulting from a transition from the $01^1 0$ level is approximately 5.7 percent as great as that of its associated band arising from the $00^0 0$ level. The tabulated values of the strengths are for both bands and other much weaker bands that may occur nearby. Isotopes other than $^{14}N_2{}^{16}O$ account for less than 1 percent of the absorption. The $01^1 2 \leftarrow 00^0 0$ band centered near 4978 cm^{-1} overlaps the $24^0 0 \leftarrow 00^0 0$ and $32^0 0 \leftarrow 00^0 0$ bands so that each of the strengths can not be determined as accurately as the sum.

The wavenumbers of the band centers are based on an article by Pliva[12], except for the $00^0 3$ band centered at 6580.83 cm^{-1}, the center of this band is from Plyler, et al.[13]. The centers of the $01^1 3 \leftarrow 01^1 0$ and $02^0 2 \leftarrow 01^1 0$ bands are not known accurately at this time, but they are displaced only a few wavenumbers from their associated bands arising from the $00^0 0$ level.

A scientific report dealing in greater detail with the absorption by the $N_2 O$ bands listed in Table 4-1 is being prepared. Included in the report are spectral transmittance curves, curves and tables of $(-1/u)\ell n\, T$, and information on the widths and shapes of the absorption lines.

TABLE 4-1

N_2O BAND STRENGTHS

Band centers cm^{-1}	Vibration levels upper	lower	Strengths (molecules^{-1} cm^2 cm^{-1}) (Multiply all values by 10^{-20}) Previous Workers	Present Work
1150.291 1168.134	03^10 02^00	01^10 00^00	44.6 (B) 40.5 (GW) 31.6 (EC)	38.5 ± 1.5
1284.907 1291.501	10^00 11^10	00^00 01^10	986 (GW) 911 (EC) 1423 (TWW)	996 ± 40
2209.523 2223.756	01^11 00^01	01^10 00^00	6880 (B) 6140 (EC) 6010 (CMT) 6930 (TWW)	5710 ± 250
2309.01 2322.57	05^10 04^00	01^10 00^00		2.7 ± 0.3
4041.397 4061.979	12^01 11^11	01^10 00^00		0.111 ± 0.006
4388.928 4417.379	01^12 00^02	01^10 00^00		6.98 ± 0.7
4612.013 4630.164	13^11 12^01	01^10 00^00		0.68 ± 0.07
4730.408 4730.828	21^11 20^01	01^10 00^00		4.40 ± 0.4
4900.97 4911.06	25^10 24^00	01^10 00^00		0.065 ± 0.006
4977.695	02^02 01^12	01^10 00^00		0.070 ± 0.008
5026.34 5029.08	32^00 33^10	00^00 01^10		0.28 ± 0.03
5105.65 5134.13	40^00 41^10	00^00 01^10		0.391 ± 0.04
6580.83	01^13 00^03	01^10 00^00		0.152 ± 0.01

(B)   Burch and Williams, Ref. 14.
(GW)   Goody and Wormell, Ref. 15.
(EC)   Eggers and Crawford, Ref. 16.
(TWW)   Thorndike, Wells and Wilson, Ref. 17.
(CMT)   Calloman, McKean, and Thompson, Ref. 18.

SECTION 5

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David A. Gryvnak
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13. ABSTRACT

The continuum absorption by H_2O between 2400 and 2780/cm^{-1} and by N_2 between 2400 and 2650 cm^{-1} has been measured. The H_2O data cover the temperature range from 338 K to 428 K and are primarily for pure H_2O. A few preliminary results for $H_2O + N_2$ mixtures are discussed. Calculated values of the continuum-absorption coefficient are compared with the experimental results. From absorption data on samples of pure N_2 and of $N_2 + O_2$ at different temperatures, the attenuation by atmospheric N_2 has been calculated for a range of temperatures encountered in the atmosphere. The strengths of several N_2O bands between 1100 and 660/cm^{-1} have been measured and are tabulated.

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KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
H_2O						
N_2O						
N_2						
Continuum						
Atmospheric Transmission						
Absorption						
Pressure Induced Absorption.						